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Helium and Radio-Activity in Rare and Common Minerals

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nodes. But the motion of the node of II can be measured, and affords the best means of finding the physical compression of Jupiter.

The fifth satellite discovered by Barnard is so near to the primary that the node of its orbit revolves through about 912° per annum, and second order terms begin to make themselves felt. A careful measurement of this motion would be of much value, for a comparison of the compression of Jupiter, deduced from the motion of the node of V with that deduced from the motion of the node of II, might provide information concerning the distribution of mass in Jupiter.

Helium and Radio-activity in Rare and Common Minerals.

By the Hon. R. J. STRUTT, F.R.S.

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CONTENTS.

PAGE
§ 1. Introduction........ 572
§ 2. Experimental Methods 575
§ 3. Statement of Experimental Results 578
§ 4. Helium and Radio-activity of Ordinary Elements 591
§ 5. Presence of Argon and Neon in Minerals 592
§ 6. Summary of Conclusions 594

§ 1. *Introduction.*

The original discovery of helium in cleveite and other minerals by Ramsay, and the subsequent explanation of its presence as due to production *in situ* by radio-active change, are of fundamental importance, and are too well known to need anything more than mention here. No exception has been known hitherto to the rule that helium is found in radio-active minerals exclusively—minerals, that is, in which either uranium, or thorium, or both, are present in appreciable quantity.

It seemed, however, that valuable information might be gleaned from a fuller examination of the subject than has yet been made.

In the first place, Rutherford has suggested with great plausibility that subatomic changes might be going on in some of the ordinary elements with emission of α particles of somewhat lower velocity than those of the radio-active elements. In such cases, owing to the abrupt disappearance of ionising and photographic action below the critical velocity, the activity

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would not make itself apparent by ordinary experimental tests. If, however, helium were a product of such a change, we might expect to find it stored up in minerals containing the element in question.

Again, as many observers have found, ionising radiation is given off by the ordinary elements. It has been supposed (and I was myself one of the first to urge that view) that this ionising radiation indicated a feeble radio-activity. The progress of knowledge has made this more doubtful than it seemed at first. One strong objection is derived from a consideration of the internal heat of the earth.* Another is derived from the want of satisfactory constancy in the amount of this ionising radiation from different samples of a metal.† It seemed that the investigation proposed might give evidence as to whether or not this ionising radiation resembled genuine radio-activity in being associated with a production of helium.

The further object was proposed of looking for argon and the other inert gases in minerals. In view of the well-known experiments of Ramsay and Cameron,‡ it is unnecessary to emphasise the interest of this question.

The result of the experiments has been that helium is found to be a nearly universal constituent of minerals, when sufficiently refined methods of isolating it are adopted. With regard to argon it is much more difficult to pronounce. The spectrum, it is true, was in nearly all cases observed.

Where the total inert residue (argon with helium) was small, the argon found was not infrequently the greater part. However, in these cases the actual quantity of argon did not usually much exceed a cubic millimetre, a quantity which would be accounted for by contamination with 1/10 c.c. of air. It is not easy to carry out the complicated manipulations involved with complete certainty of excluding this amount of leakage. However, in the case of a few minerals, much less argon than this was observed, so that such leakage is not inevitable. I do not doubt that by careful working and with many repetitions the question of whether argon is commonly present in minerals to the extent of 1 cubic millimetre per kilogramme could be settled. In the case of igneous rocks it certainly *is* present in larger quantities than this, and I believe that the same is true of certain other siliceous materials, but further examination is required.

In the case of helium, no uncertainty of this kind is encountered. For it is only present in the air in infinitesimal proportions.

In determining whether or not the helium present in a mineral can be attributed to traces of the radio-active elements, I apply, in the first place, the crude test of comparison with the strongly radio-active minerals, in which helium is certainly derived from that source. If the quantity of helium should not be greater relatively to the radium than in such minerals, there is no *primâ facie* reason to look further for its origin. The radium in a mineral is proportional to the uranium contained in it, and, when known, allows the latter to be calculated. Both, in all probability, contribute to the helium present, and a more convenient unit is obtained by computing the volume of helium per gramme of uranium oxide than by expressing it relatively to the radium content. I shall call this, for brevity, the helium ratio.

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* 'Nature,' December 21, 1905.

† 'Phil. Mag.,' June, 1903. Also MacLennan, 'Phil. Mag.,' [6], vol. 14, p. 760, 1907.

‡ 'Chem. Soc. Proc.,' vol. 91, p. 1593, 1907.

Many of the strongly active minerals contain thorium, which also contributes to the helium contained.* In such cases, the ratio of helium to uranium may be much higher than in those where the uranium series is of chief importance. In establishing the normal helium ratio I shall ignore the former class.

It would scarcely be feasible to determine the probably very minute amount of thorium in the common minerals and ores; but it will appear in the sequel that the results of the present paper are not, as it happens, rendered difficult of interpretation by this circumstance.

The amount of helium found in the minerals will, of course, depend on the time which has elapsed since their formation, and is accordingly limited by the geological age of the strata in which they occur. It is unfortunate that geological evidence as to the age of metalliferous veins is usually vague; nor can it even be regarded as certain that all the minerals in the same vein are approximately contemporary. Further, we cannot be sure that all the helium which has been generated in the minerals still remains there. A part may have escaped. For these reasons the present investigation has no claim to be regarded as strictly quantitative. Nearly all the minerals examined occur in palæozoic rocks, and, except in a few extreme cases, I shall not attempt to distinguish the geologically older minerals from the geologically younger ones. The object of the investigation is to test materials of widely diverse chemical nature. To attain this it is necessary to be content with but vague information as to their geological age. Nevertheless, the general result will, I think, be regarded as fairly clear when the data given in this paper are examined.

The very interesting problem of tracing the effect of geological age on the helium ratio must be left for future treatment. Such materials as limestones suggest themselves as suitable for this investigation.

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* 'Roy. Soc. Proc.,' A, vol. 80, p. 56.

§ 2. *Experimental Methods.*

To extract helium from a mineral, we have the choice of two methods. The gas may be extracted by chemical disintegration of the material, or by heat. In the present case it was desired to look for helium present in very minute proportions, and to do this adequately it was necessary to extract the gas from large quantities of material, in some cases as much as 1 kilogramme or even more. It is scarcely feasible to decompose chemically such quantities of refractory minerals, when the onerous condition of working in a perfectly air-tight apparatus has to be observed. I have, therefore, contented myself with the summary method of heating the minerals to redness. It is true that the whole of the helium is not liberated in this way, but, for a pioneering investigation like the present, it was considered sufficient to assume that the quantity extracted by heat was half the total, as in the case of cleveite and kindred minerals.*

When less than 200 grammes of the mineral was to be heated, tubes of hard glass were used. For larger quantities it was found convenient to use weldless steel tubing, such as is used for building the frames of bicycles and motor cars. The tube was closed at one end with a cap turned out of rolled brass and soldered on to the steel with silver solder.† The steel tube was heated either in a gas furnace or, what is better, by electrical means. In the latter case the tube was wrapped in asbestos paper, and over this was wound a helix of nickel wire, through which the heating current could be passed. Over this was a thick layer of asbestos for heat insulation.

A glass exit tube was connected to the steel tube by means of a rubber cork, which was jacketed externally with water. This jacket served the double purpose of preventing any inward leakage of air under exhaustion and of protecting the rubber from injury by heat conducted along the hot metal.

The powdered mineral was placed in the steel tube, which was exhausted by a mercury pump. After it had stood exhausted all night, a little oxygen was added, and removed by the pump, so as to wash out all traces of air. Heat was then applied to drive off the gases contained. These gases passed over potash, then hot copper oxide, then over potash again, finally over phosphoric anhydride. These reagents absorbed most of the hydrogen and oxides of carbon evolved. The gas which passed them was collected through

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* Travers, 'Roy. Soc. Proc.,' vol. 64, p. 141, 1898.

† It is found much easier in practice to close the tube air-tight with a cap than with a plug.

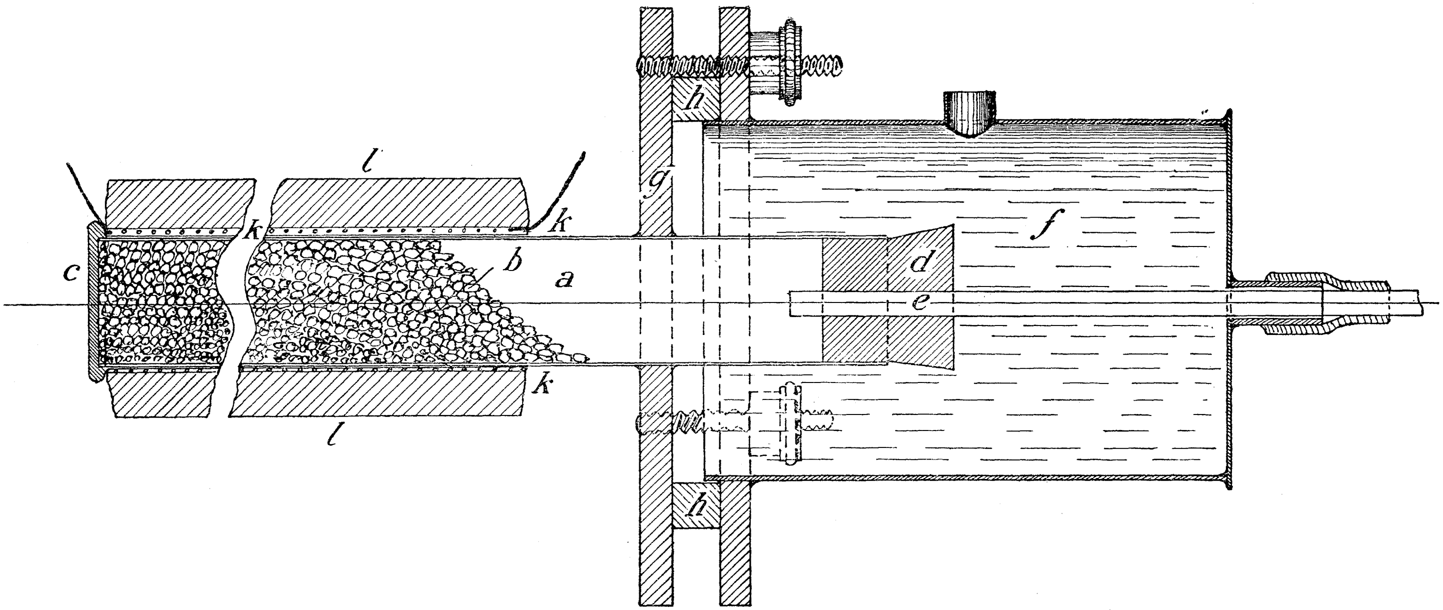

FIG. 1.—Retort used for extracting gases from minerals by heat. *a*, Weldless steel tube containing the powdered mineral *b*, and closed air-tight at one end by the brass cap *c*, hard soldered on, and at other end by rubber cork *d*; *e*, glass tube for extraction of gas; *f*, water-jacket closed by the plate *g*, soldered on to *a*. The joint is made water-tight by the rubber ring *hh*. The retort is heated by the resistance coil *kk*, of nickel wire, insulated by asbestos paper, and surrounded by the asbestos jacket *ll*.

the pump. When the tube had been kept at a full red heat for two hours,* practically nothing more could be extracted.

The gas thus collected consisted chiefly of nitrogen, which exists in nearly all the minerals examined. To remove this nitrogen, sparking with oxygen was resorted to. The operation was carried out over mercury, in a eudiometer with wires sealed in at the top, which very nearly touched one another. A fragment of solid potash, partially hydrated, floated on the top of the mercury. The spark, or rather arc, was produced by a Ruhmkorff coil with an alternating current in the primary. The electrodes being fixed, the arc cannot be conveniently started by approximating them. The starting was effected by allowing the hammer of the coil to vibrate in synchronism with the supply, which it readily did, producing a spark, as when a battery is in use. The spark soon degenerated into an arc, and the hammer then ceased to vibrate. The primary current was promptly diminished by resistance, so that the arc should not be large enough to risk melting the electrodes or cracking the glass. Oxidation and removal of nitrogen then proceeded without attention. It is much better not to hurry the process by increasing the current. With a small arc there is little danger of any accident involving loss of the gas. After contraction was over the excess of oxygen was removed by melted phosphorus, after the method of Ramsay and Travers.

In the majority of cases, where the quantity of inert gas was inconsiderable, the residue left after absorption by phosphorus amounted to something like 10 to 30 cubic millimetres, which was still a considerable multiple of the volume of the inert gases. It seems scarcely feasible to isolate minute quantities of these gases perfectly by the method of sparking, though I have not paid particular attention to the causes of failure. The final purification was effected in the vacuum tube in which the gas was to be spectroscopically examined. This tube was provided with electrodes of the liquid alloy of sodium and potassium, which, under the influence of the discharge, absorbs all traces of nitrogen, hydrogen, and carbon compounds. I am indebted for the knowledge of this invaluable method to Sir James Dewar. It has also been described by Mey.† After the gas in the vacuum tube had been sparked for a few minutes, the spectrum showed nothing but the inert gases. Helium was usually conspicuous at this stage. Argon, however, was rarely, if ever, completely absent from the spectrum. To isolate helium, Sir James Dewar's admirable method of absorption with cooled charcoal was employed. I have found that cooling to −80°, with carbonic acid snow in alcohol, suffices for the purpose when the quantity of gas to be absorbed is small. This is a great convenience in a laboratory which is not provided with the means of producing liquid air.

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* The closed end must not be raised to more than a dull red heat, for the sake of the soldered joint.

† 'Verhand. Deutschen Phys. Gesellschaft,' vol. 5, p. 72, 1903.

Connection was opened between the vacuum tube and a small vessel containing cocoanut charcoal at −80° C., which had been freed from occluded gases by preliminary heating and exhaustion. In a few minutes the spectrum of argon became practically invisible. In most cases a brilliant helium spectrum remained.* In order to measure the volume of the inert gases, either before or after the charcoal separation, a modified McLeod gauge was used, so arranged that the gas could be drawn into it from the rest of the apparatus, or replaced. The bulb of the McLeod gauge had a volume very large compared with the vacuum tube and charcoal reservoir. Thus nearly all the gas could be drawn into it when the mercury was lowered. The construction and method of manipulation will be apparent from fig. 2, with the explanation appended.

Until we know how much of the known radio-active bodies are present in a mineral, it is obviously impossible to say how far the helium in it may be derived from any other source. For this reason it formed an essential part of the present investigation to determine the quantity of radium in each of the minerals examined. The nearly universal presence of this element in rock-forming minerals† justified a suspicion that it would also be found in metalliferous ores, as well as in other siliceous minerals. This anticipation has been confirmed. The methods used for determining radium were those described in a former paper.‡

§ 3. *Statement of Experimental Results.*

This first set of results refers to minerals which are quite strongly radio-active and (for the most part) quite rich in helium. These results are taken from a former paper§ and are given here for convenience only. They seem to establish a kind of scale which shows roughly what ratio is to be expected between helium in a mineral and the uranium it contains. Many radio-active minerals contain considerable quantities of thorium, and in these cases the ratio is higher than usual. In this list only those minerals in which the uranium series contributes the greater part of the activity

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* When the quantity of argon was appreciable, as in igneous rocks, the charcoal treatment had to be repeated more than once.

† 'Roy. Soc. Proc.,' A, vol. 78, p. 152.

‡ 'Roy. Soc. Proc.,' A, vol. 77, p. 474.

§ 'Roy. Soc. Proc.,' March 2, 1905.

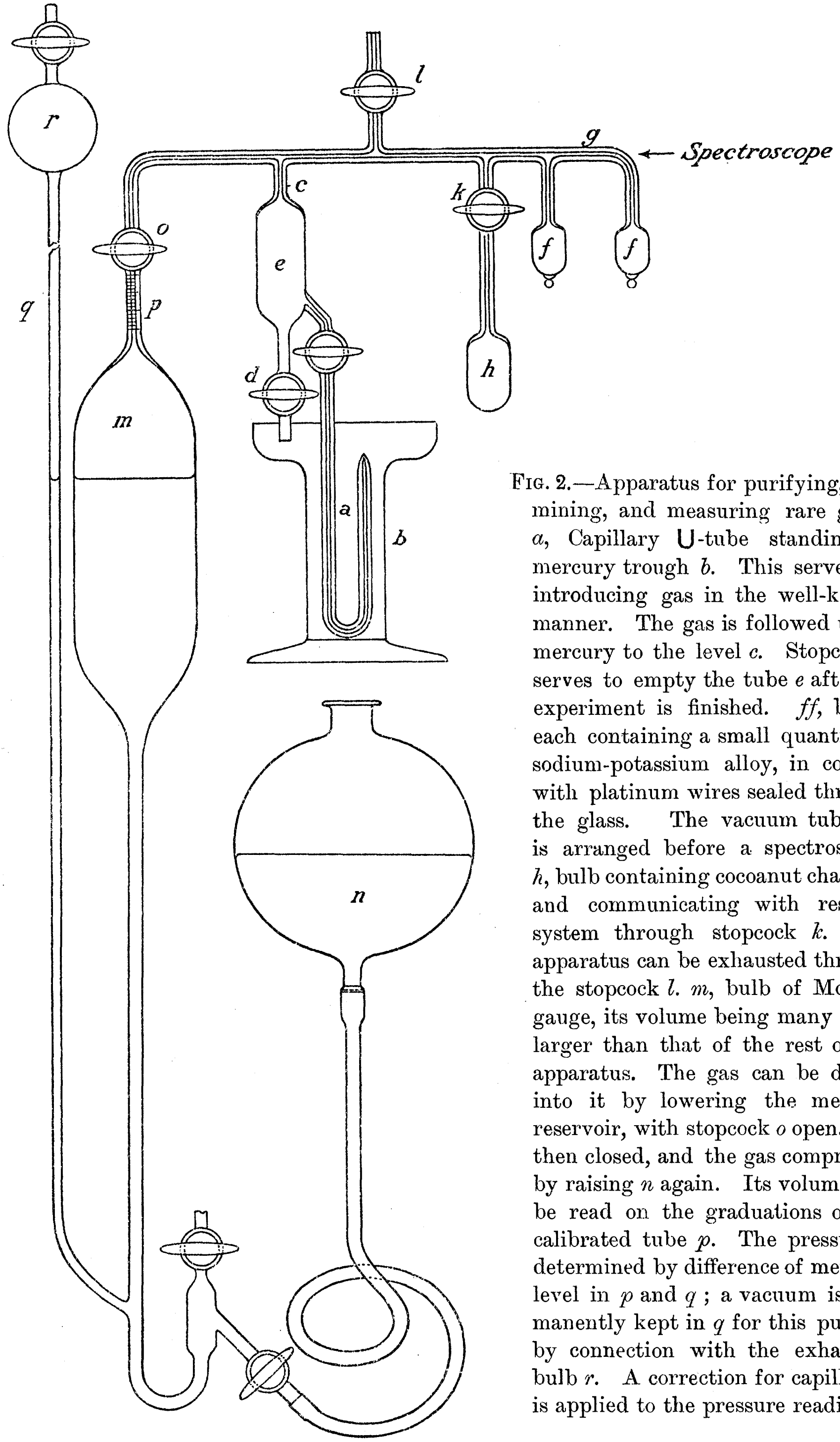

Fig. 2.—Apparatus for purifying, examining, and measuring rare gases. *a*, Capillary U-tube standing in mercury trough *b*. This serves for introducing gas in the well-known manner. The gas is followed up by mercury to the level *c*. Stopcock *d* serves to empty the tube *e* after an experiment is finished. *ff*, bulbs, each containing a small quantity of sodium-potassium alloy, in contact with platinum wires sealed through the glass. The vacuum tube *fgf* is arranged before a spectroscope. *h*, bulb containing cocoanut charcoal, and communicating with rest of system through stopcock *k*. The apparatus can be exhausted through the stopcock *l*. *m*, bulb of McLeod gauge, its volume being many times larger than that of the rest of the apparatus. The gas can be drawn into it by lowering the mercury reservoir, with stopcock *o* open. *o* is then closed, and the gas compressed by raising *n* again. Its volume can be read on the graduations of the calibrated tube *p*. The pressure is determined by difference of mercury level in *p* and *q*; a vacuum is permanently kept in *q* for this purpose by connection with the exhausted bulb *r*. A correction for capillarity is applied to the pressure readings.

are given. I have also excluded substances like torbernite and carnotite, which are obviously of secondary and quite recent origin.

Table I.

Mineral.	Locality.	Helium, c.c. per gramme.	Grammes uranium oxide (U_3O_8) per 100 grammes.	c.c. helium per gramme uranium oxide.
Pitchblende	Joachimsthal	0·107	73·5	0·146
Pitchblende	St. Stephen's Mine, Cornwall	0·10	21·23	0·472
Æschynite	Hitteroe, Norway	1·09	9·42	11·6
Samarskite	N. Carolina	1·5	10·3	14·5
Cyrtolite	Llano, co. Texas	1·15	3·67	31·4
Sipilite	Little Friar Mt., Virginia	0·59	2·86	20·7
Euxenite	Arendal, Norway	0·73	2·84	25·7
Microlite	Amelia Court House, Virginia	0·05	1·89	2·64

The results quoted show that 10 is a normal value for the helium ratio, though values as high as 30 occur. The low value for pitchblende has long seemed anomalous, and will not appear less so in comparison with the results of the present paper, showing normal values for most of the other Cornish vein-minerals.

Table II gives a list of results for minerals containing the rare earths and some other rare elements. It will be noticed that the helium content is in several cases in excess of what the uranium present can account for, and in one case (fluor from Ivitgut, Greenland) enormously in excess.* I regard this excess of helium as due to the radio-activity of thorium contained in the mineral. In all the cases marked thus † thorium was looked for and detected by its emanation. Although no strictly quantitative experiments were made, the amount of thorium emanation appeared amply sufficient to account for the helium present.

I have failed to find minerals containing the rare earths which are reasonably free from both uranium and thorium. Accordingly a good deal of helium is always present, and it is impossible to be sure that a part of it is not contributed by other constituents such as cerium. But the determinations afford no positive support for such a view, and any such contribution must be very small compared with the contribution made by an equal mass of uranium or thorium.

In none of these cases was evidence obtained of the presence of rare gases other than helium. If any argon or neon was present, its quantity must have been quite insignificant in comparison. The inert residue always gave the brilliant yellow glow of pure helium.

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* See 'Roy. Soc. Proc.,' A, vol. 80, p. 56.

Table II.—Rare Earth Minerals. Less Active Class.

Mineral, with list of principal constituents.	Locality.	Quantity taken, grammes.	Helium extracted by heat, c. mm.	Helium extracted by heat, c. mm. per 100 grammes.	Grammes radium per 100 grammes.	Grammes uranium oxide per 100 grammes, calculated.	Helium ratio.
Zircon, Zr.Si.O	Kimberley..............	55	6·77	12·3	$1{\cdot}91 \times 10^{-9}$	$5{\cdot}9 \times 10^{-3}$	4·4
Eudialite, Zr.Ca.FeSiO	Greenland..............	74	108	146	$1{\cdot}26 \times 10^{-9}$	$3{\cdot}9 \times 10^{-3}$	81·0†
Orthite, Ce.La.Yt.Al.FeSi.O	Sweden	25	55	220	$2{\cdot}36 \times 10^{-8}$	$7{\cdot}3 \times 10^{-2}$	6·6
Gadolinite, Yt.Ce.Fe.SiO	Hitteroe, Norway ...	36	380	1050	$1{\cdot}36 \times 10^{-8}$	$4{\cdot}2 \times 10^{-2}$	50·0†
Keilhauite, Yt.Ti.Ca.Al.FeSi.O ...	Alve, Norway	16	260	1630	$4{\cdot}52 \times 10^{-8}$	$1{\cdot}4 \times 10^{-1}$	23·0
Niobite, Nb.Ta.Fe.O	Haddam, Connecticut	125	450	360	$9{\cdot}7 \times 10^{-9}$	$3{\cdot}0 \times 10^{-2}$	5·7
Apatite, Ca.P.O.F., with traces of Ce, etc.	Canada	240	280	116	$1{\cdot}46 \times 10^{-9}$	$4{\cdot}5 \times 10^{-3}$	53·0†
Fluor, with rare elements...........	Ivitgut, Greenland ...	1000	27,000*	2700	$1{\cdot}58 \times 10^{-10}$	$4{\cdot}9 \times 10^{-4}$	5600†
Cerite, Ce.La.Dy.Si.H.O	Bastnaes, Sweden ...	65	82	126	$3{\cdot}0 \times 10^{-9}$	$9{\cdot}3 \times 10^{-3}$	27

* Determination by Professor Julius Thomsen.

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Tables III, IV, V include a selection of minerals of varied composition, for the most part containing only traces of uranium. The helium is never distinctly in excess of what uranium and its products will account for. It should be explained that a good many of the experiments were made before any adequate apparatus had been set up for quantitative measurement. Helium, qualitatively observed, is entered as He. In such cases the quantity was not at most in excess of 2 cubic millimetres, judging by the appearance of the discharge. Usually it was very much less.

With regard to argon, the spectrum was generally seen, but the quantity was never more than 2 cubic millimetres, and never in excess of probable contamination from air.

Where the quantity of helium was insignificant, the argon spectrum was comparable with it in intensity. In such cases a query is entered under argon, to show that it may possibly occur in quantity comparable with helium. Where helium was more abundant, the argon spectrum was always inconspicuous. To distinguish these cases argon is entered as 0. But it must be repeated that there is no evidence of its presence in either of these cases.

It would seem probable that the minerals in these tables are very free from thorium. They occur for the most part in mineral veins and ore deposits, being contrasted in this respect with many of those in Tables I and II, which are primary constituents of igneous rocks.

Thorium was specially looked for in wolfram, but was not found.

The next set of experiments refers to igneous rocks. It will be observed that the helium ratio is of the same order as usual. The Irish basalt was erupted in tertiary times, and solidified long after the formation of the majority of minerals examined. However, as pointed out in a previous paper, a part of the helium now present was in all probability dissolved or entangled in the original magma. It is worthy of remark that the Cornish granite shows a considerably smaller ratio than some of the minerals of the veins which traverse it, and which are clearly younger. This may, perhaps, be partly due to the fact that a great part of the radio-active material in this granite is contained in the mica, which from its structure may be unable to retain helium. However, in view of the imperfect extraction of helium from some minerals by heat, anomalies of this kind must be expected in any case. As already mentioned, it is hoped to study the subject in this aspect later.

The quantities of argon found in these rocks are considerably smaller than those given formerly.* This is to be explained by the imperfection of the experimental method then adopted. It was assumed that after sparking

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* 'Roy. Soc. Proc.,' A, vol. 79, p. 436.

Table III.—Sulphides, Selenides, and Arsenides.

Mineral, with list of principal constituents.	Locality.	Quantity taken, grammes.	Helium extracted by heat, c. mm.	Argon extracted by heat, c. mm.	Grammes radium per 100 grammes.	Grammes uranium oxide per 100 grammes, calculated.	c.c. helium per gramme uranium oxide.
Galena, Pb.S	Nenthead, Cumberland	1187	0·9	?	$2·91 \times 10^{-12}$	$9·0 \times 10^{-6}$	17
Smaltite, Co.As	... ...	277	He	?	$1·46 \times 10^{-10}$	$4·5 \times 10^{-4}$	—
Cinnabar, Hg.S	Almaden, Spain	100	0	0	—	—	—
Bornite, Cu.Fe.S	Cornwall	259	30·5	0	$1·04 \times 10^{-9}$	$3·2 \times 10^{-3}$	7·4
Stibnite, Sb.S	New South Wales	225	1·6	?	$4·20 \times 10^{-11}$	$1·3 \times 10^{-4}$	7·8
Clausthalite, Pb.Se	Cacheuta, Mexico	36	He	?	—	—	—
Molybdenite, Mo.S	Renfrew, co. Ontario, Canada	96	He	?	—	Ra	—
Blende, Zn.S	Minerva Mine, Wrexham, Denbigh	560	0·37	?	$2·27 \times 10^{-11}$	7×10^{-5}	2·0
Blende, Zn.S (In)	Freiberg	40	He	?	—	—	—
Blende, Zn.S (Ga)	Bensberg	150	He	?	—	—	—
Lorandite, Tl.As.S..............	... ...	1·5	He	?	—	—	—
Tin pyrites, Sn.Cu.Zn.Fe.S ...	Cornwall	317	1·45	?	$1·00 \times 10^{-11}$	$3·1 \times 10^{-5}$	29
Argyrodite, Ag.Ge.S............	Freiberg	0·7	He	?	—	—	—
Cadmium Blende, Cd.S	Prisbran, Bohemia	10	He	?	—	—	—

Table IV.—Native Elements and Oxides.

Mineral, with list of principal constituents.	Locality.	Quantity taken, grammes.	Helium extracted by heat, c. mm.	Argon extracted by heat, c. mm.	Grammes radium per 100 grammes.	Grammes uranium oxide per 100 grammes.	c.c. helium per gramme uranium oxide.
Silver, Ag	Broken Hill, New South Wales......	43	He	?	—	—	—
Iron, Fe	Meteorite of Augusta, co. Virginia	400	<0·66	?	$2·52 \times 10^{-12}$	$7·8 \times 10^{-6}$	<42
Iron, Fe	Ovifak, Disco Island, Greenland ...	412	<0·97	?	$2·23 \times 10^{-11}$	$6·9 \times 10^{-5}$	< 3·3
Bismuth, Bi	Australia	30	He	?	—	—	—
Tellurium, Te............	Facebay, Transylvania	8	He	?	—	—	—
Graphite, C	Borrodaile, Cumberland	232	8·5	0	$3·26 \times 10^{-10}$	$1·1 \times 10^{-3}$	6·7
Hæmatite, FeO	Cumberland	446	32·4	0	$5·06 \times 10^{-10}$	$1·57 \times 10^{-3}$	9·0
Cassiterite, SnO............	St. Austell, Cornwall	775	29·0	0	$1·26 \times 10^{-10}$	$3·9 \times 10^{-4}$	19
Chromite, Cr.Fe.O......	Unst, Shetland............	250	He	?	—	—	—
Ilmenite, Ti.FeO	Egasund, Norway	250	He	?	—	—	—
Cuprite, CuO	Wheal Phœnix, Cornwall	250	He	?	Ra	Ur	—
Corundum, AlO.........	Iredell, co. Statesville, N. Carolina	200	He	?	Ra	Ur	—

Table V.—Miscellaneous.

Mineral, with list of principal constituents.	Locality.	Quantity taken, grammes.	Helium extracted by heat, c. mm.	Argon extracted by heat, c. mm.	Grammes radium per 100 grammes.	Grammes uranium oxide per 100 grammes, calculated.	c.c. helium per gramme uranium oxide.
Wolfram, W.Fe.O	East Pod Mine, Illogan, Cornwall	207	240	0	$3 \cdot 39 \times 10^{-9}$	$1 \cdot 05 \times 10^{-2}$	22
Scheelite, W.Ca.O	Cornwall	40	He	?	—	—	—
Vanadinite, V.Pb.O	Dumfries	300	0	?	—	—	—
Triphylene, Li.Mn.P.O...	Grafton, New Hampshire	310	He	?	—	—	—
Barytes, Ba.S.O	Pallaflat, St. Bees, Cumberland...	500	0·42	?	$1 \cdot 42 \times 10^{-10}$	$4 \cdot 4 \times 10^{-4}$	0·38
Celestine, SrS.O	Zate, Gloucestershire	1825	0·75	?	$8 \cdot 39 \times 10^{-11}$	$2 \cdot 6 \times 10^{-4}$	0·27
Fluor spar, CaF...........	Wheal Mary Anne, Cornwall ...	250	He	?	—	—	—
Calcite, Ca.C.O	Cumberland	1289	$<0 \cdot 74$	?	$7 \cdot 10 \times 10^{-12}$	$2 \cdot 2 \times 10^{-5}$	$<5 \cdot 4$
Embolite, Ag.Br.Cl	Broken Hill, New South Wales...	20	He	?	—	—	—
Iodyrite, Ag.I..............	Broken Hill, New South Wales...	30	He	?	—	—	—

Table VI.—Igneous Rocks.

Rock.	Locality.	Quantity taken, grammes.	Helium extracted by heat, c. mm.	Argon extracted by heat, c. mm.	Grammes radium per 100 grammes.	Grammes uranium oxide per 100 grammes, calculated.	c.c. helium per gramme uranium oxide.
Granite	Cornwall	660	19·0	7·5	$2{\cdot}81 \times 10^{-10}$	$8{\cdot}7 \times 10^{-4}$	6·66
Diorite	Mt. Sorrel, Leicestershire	1200	6·24	20·3	$6{\cdot}45 \times 10^{-11}$	$2{\cdot}0 \times 10^{-4}$	5·2
Phonolite	Trafrain Law, Haddingtonshire	820	7·1	10·8	—	—	—
Basalt	Ireland	1190	2·25	3·0	$6{\cdot}13 \times 10^{-11}$	$1{\cdot}9 \times 10^{-4}$	2·0

and removal of oxygen the residue might be measured as argon + helium. Further experiment has shown that the volume measured after the spectroscopic purification in the vacuum tube itself is much smaller. This, of course, only applies to very small volumes of gas. Large volumes can readily be purified by sparking.

Table VII gives results for siliceous minerals other than igneous rocks. In no case is the quantity of helium considerable, and in no case is there reason to regard it as proceeding from any other source than the uranium series. In view of the small quantity of uranium and radium in quartz, this mineral affords a severe test case for the possible production of helium from common elements.

It will be noted that flint from the upper chalk, which is geologically recent compared with most of the materials examined, shows, in accordance with anticipation, a very much lower helium ratio.

In the several samples of quartz examined, there seems to be evidence of the presence of argon in excess of what can be explained by atmospheric contamination, though the margin is not large. In garnierite, the presence of argon seems certain. The determination quoted is only one of several, all of which were believed to be unexceptionable, and all of which pointed to about the same quantity. I am inclined to suspect that the presence of traces of argon in siliceous material is general, though certainty could only be achieved with great labour. Something more will be said on this subject in a later paragraph.

The first four sets of determinations in Table VII, which are only samples of many similar ones, refer to the mineral beryl. This mineral has proved altogether exceptional. It will be observed that the helium present is, as a rule, enormously in excess of what can be attributed to uranium and its series. This raises the question of whether thorium is present. For this, as for further investigations on the subject, I used the beryl richest in helium, that found at Acworth, New Hampshire.*

Thorium emanation could, indeed, be just detected by careful experiments in a considerable quantity (50 grammes) of Acworth beryl in solution. But the thorium series does not appear to contribute more, if so much, to the total radio-activity of the mineral as does the uranium series, and affords no explanation of the quantity of helium present.

With the idea that some unknown radio-active constituent might be present which did not yield an emanation, the powdered beryl was carefully tested with an electroscope for radio-activity. Nothing could be detected,

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* Another sample of beryl from the same place, somewhat more transparent than the foregoing, contained much less helium.

Table VII.—Silica and Silicates.

Mineral, with list of principal constituents.	Locality.	Quantity taken, grammes.	Helium extracted by heat, c. mm.	Helium extracted by heat, c. mm. per 100 grammes.	Argon extracted by heat, c. mm.	Grammes radium per 100 grammes.	Grammes uranium oxide per 100 grammes.	c.c. helium per gramme uranium oxide.
Quartz, Si.O	Madagascar	1250	2·4	0·192	3·16	$1·39 \times 10^{-11}$	$4·29 \times 10^{-5}$	9·0
Quartz, Si.O	From veins in slate, Ilfracombe	1187	1·43	0·121	2·5	$7·45 \times 10^{-12}$	$2·31 \times 10^{-5}$	10·4
Quartz, Si.O	Brazil	1015	0·74	0·073	2·0	—	—	—
Quartz sand, Si.O ...	... ...	300	0·55	0·183	?	$1·94 \times 10^{-11}$	$6·0 \times 10^{-5}$	6·0
Flint, Si.O	From chalk, Brandon, Norfolk	1275	0·295	0·023	1·9	$4·30 \times 10^{-11}$	$1·33 \times 10^{-4}$	0·246
Garnierite, Ni.Si.O.H	Oregon	920	2·5	0·272	6·4	—	—	—
Lepidolite, LiAlSi (Rb) (Cs) O	Auburn, Maine, U.S.A.	250	He	—	?	—	—	—
Rhodonite, Mn.Si.O	Cornwall	182	He	—	?	$1·49 \times 10^{-10}$	$4·6 \times 10^{-4}$	—
Topaz, Al.Si.O.F ...	Brazil	50	He	—	?	—	—	—
Orthoclase, KAlSiO	Glass Mine, Rocks, Cornwall	250	He	—	?	Ra	—	—
Spodumene, LiAlSiO	Brazil	10	He	—	?	—	—	—
Pollux, Cs.AlSiO ...	Hebron, Maine	2	0	—	0	—	—	—
Tourmaline, Al.B. Mg.SiO, etc.	Madagascar	230	He	—	?	Ra	—	—

though other minerals containing much less helium showed a conspicuous activity when tested in this manner, in virtue of the radio-active constituents present. The following results illustrate this.

A correction for the ordinary leak of the electroscope (0·40 div. per hour) has been applied.

Mineral.	Helium, c.c. per 100 grammes.	Rate of electroscope leak. Scale div. per hour.
Beryl	1·68	0·03 ?
Niobite	0·36	8·45
Cerite	0·13	0·86
Zircon	0·12	1·05
Wolfram	0·12	0·46

Thus it appears impossible to connect the helium in beryl with radio-activity in the ordinary sense of the word.

It was next attempted to see if helium in comparatively large quantities could be connected with any recognised constituent of beryl, without regard to radio-activity. Beryllium seemed the most promising constituent. Several other beryllium minerals such as phenacite and chrysoberyl, were tried, as recorded above. But only those traces of helium were found which are almost universal, and which I attribute to traces of the radio-active elements. Cæsium has been found in some beryls, but the absence of helium from the cæsium mineral, pollux (see Table VII), makes it unlikely that this element is concerned. Moreover, the cæsium lines were not visible in the flame spectrum of my beryl. The remaining important constituents of beryl are comparatively common, and are amply represented in the tables of minerals given above, so that they, too, must be excluded. Examination of the flame spectrum of Acworth beryl revealed the presence of indium, but in less quantity than in Freiberg blende; and Freiberg blende yields little helium.

The above paragraphs summarise the experimental evidence which I have been able to obtain on this question, without affording any positive answer to it. It is difficult to find any advantageous ground from which to attack it further.

A few words may be said on some possible explanations:—

(1) It may be suggested that these beryls have formerly contained radio-active elements, but that these have now decayed, their transformations being completed.

The objection to this view is that nearly all the evidence we have points to an unalterable rate of radio-active transformation. Thus the explanation

Table VIII.—Beryls and other Beryllium Minerals.

Mineral, with list of constituents.	Locality.	Quantity taken, grammes.	Helium extracted by heat, c. mm.	Argon extracted by heat, c. mm.	Grammes radium per 100 grammes.	Grammes uranium oxide per 100 grammes.	c.c. helium per gramme uranium oxide.
Beryl, Be.Al.SiO.Li ...	Acworth, New Hampshire	250	4200	0	$1 \cdot 13 \times 10^{-9}$	$3 \cdot 5 \times 10^{-3}$	954
Beryl ,, ...	Chester, Pennsylvania.................	81	550	0	$7 \cdot 10 \times 10^{-10}$	$2 \cdot 2 \times 10^{-3}$	620
Beryl ,, ...	Arendal, Norway.......................	63	153	0	$2 \cdot 39 \times 10^{-9}$	$7 \cdot 4 \times 10^{-3}$	66
Beryl ,, ...	Massachusetts, U.S.A..................	16	5·1	0	$3 \cdot 23 \times 10^{-11}$	$1 \cdot 0 \times 10^{-4}$	628
Phenacite, Be.SiO ...	Takavaya, Siberia.......................	38	(He)	?	—	—	—
*Chrysoberyl, BeAlO ...	Ceylon	52	He	?	—	—	—
Chrysoberyl ,, ...	Haddam, Connecticut	65	He	?	—	—	—
Melliphanite, Be.Al. Ca.SiO	Brevig	9	He	?	—	—	—
Beryllonite, Be.NaP.O	Stoneham, Maine.......................	9	He	?	—	—	—

mentioned would require the assumption that beryls generally were much older than other minerals of the earth's crust. The circumstances of their occurrence, geologically considered, are not consistent with this assumption.

(2) It may be supposed that the helium found in beryls was not generated *in situ* at all, but was chemically absorbed or occluded by the material in the course of solidification. I cannot think this in any way probable. Other siliceous minerals do not absorb helium in this way, for they contain none that may not be otherwise accounted for. Nor does anything we know of the properties of helium suggest that it is likely to have a violent preference for beryl.

(3) There may be an unknown element present in beryl which has escaped detection, for want of well marked chemical peculiarities; and this unknown element may emit α-particles with less than the critical velocity, as suggested in the introduction (p. 572). On this double hypothesis the facts would be explained. But naturally an explanation so speculative has in itself little scientific value.

§ 4.—*Helium and Radio-activity of Ordinary Elements.*

The results above recorded are not in favour of the theory that the common elements are perceptibly radio-active. This seems clear from the following considerations. It is known that radium, actinium, and thorium* give rise to helium. There is no evidence which to me, at least, appears convincing that any one of the undoubtedly radio-active bodies does not give rise to it. Accordingly, we may provisionally regard the formation of helium as a criterion of radio-activity.

It is well known that there is an ionising radiation from the walls of any vessel which ionises the contained air. The question to be faced is whether any important part of this radiation is of the same nature as the α-rays of radium.

In determining the radium content of galena (see Table III), 200 grammes of the mineral were stored in solution, so as to allow the emanation to accumulate. The emanation was boiled out and introduced into an electroscope and allowed to form the active deposit. After this the leak of the electroscope was increased by about one-quarter of its normal amount. Now this increased leak is of the same order as the total ionising power of the uranium series of bodies present in 200 grammes of the mineral, when exercised freely, without enfeeblement, owing to unproductive absorption of the rays by solids. The electroscope case was a glass bulb 10 cm. in diameter, or about 314 sq. cm. in area. As the α-rays are not able to penetrate from a depth of more than about 0·004 cm., it follows that the total quantity of glass which can come into action in ionising the enclosed air cannot be much more than 314 × 0·004 c.c., or about 3·5 grammes. The ionisation produced by this quantity of glass is greater than that produced by the radio-active impurities in 200 grammes of galena. The normal ionisation in vessels of other common materials is not very different. It may be concluded that in a mineral like this galena the apparent activity contributed by the common elements (lead and sulphur) is at least a hundred times that due to the radio-active impurities. As these impurities are present in sufficient quantity to account for the helium found, it follows that enormously larger quantities of helium would be expected if the ionising properties of the common elements were really of radio-active origin.

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* 'Roy. Soc. Proc.,' A, vol. 80, p. 56.

The lists of results which have been given afford many other cases of minerals free enough from radium to emphasise the same conclusion. There is no indication that the helium ratio increases as the radio-active impurities diminish in amount.*

It is evidently of great interest to push the enquiry into possible helium production by common elements as far as possible; for although their radio-activity seems to be much smaller than might be expected from the ionising power, it is not, for that reason, necessarily non-existent.

I have found that gypsum, rock salt, and the various saline minerals of Stassfurt are for the most part much less contaminated with radium than minerals of any other class. In most cases helium can scarcely be detected in them; but in one or two instances results have been obtained which call for further investigation. It is hoped to complete these experiments shortly.

§ 5. *Presence of Argon and Neon in Minerals.*

The interest of this subject has already been referred to. It has been recorded that siliceous materials in general appear to contain a little argon, and that igneous rocks certainly always do so. The question now arises of whether the argon is due to radio-active changes, as might appear not improbable from Sir William Ramsay and Mr. Cameron's results.

It might perhaps be supposed that the conditions of radio-active change were so modified in these materials as to result in the partial substitution of argon for helium. Upon the whole I do not regard this supposition favourably. In siliceous minerals like zircon, which are fairly active, the argon content is infinitesimal in comparison with the helium content. This appears from the experiments already quoted. Some other experiments, specially directed to this point, which were made before the systematic investigations here recorded, bring it out more clearly: 12·8 c.c. of helium was extracted by heating a large quantity of zircon. The argon contained in this was separated by charcoal cooled in liquid air, and was certainly less than 0·03 c.c. Again, 37·6 c.c. of helium from cyrtolite, another radio-active silicate, contained at most 0·02 c.c. argon. In these cases, therefore, the argon does not greatly exceed a thousandth part of the helium and may be much less, for the experiments were made before very much experience had been gained, and considerable atmospheric contamination is not improbable. The quantity of argon in active silicates is not large,* and it may be concluded that it is not connected with their activity. Similar experiments made with large quantities of helium from monazite, samarskite, and thorianite proved that the argon in these cases did not at most exceed a thousandth part of the helium.

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* It seems likely from the results of MacLennan ('Phil. Mag.,' [6], vol. 14, p. 760, 1907) and Elster and Geitel, that other samples of galena will be found much less free from radio-active impurities than that which I examined. For their results point to great variety in the quantities of polonium in various samples of commercial sheet lead.

The small quantities of argon in question may, I think, be very well regarded as derived from the atmosphere during the formation of the various minerals.

With regard to neon, the available data are very scanty. Its presence was, as a rule, masked by helium which, when present in excess, altogether extinguishes the yellow neon line. The difficulty can be overcome by separation with charcoal in liquid air. This has not usually been available to me, and carbonic acid cooling does not suffice for the absorption of neon. In a few cases of igneous rocks, neon has been observed as recorded in a former paper.† I separated spectroscopic traces of neon from the small quantity of argon from zircon and cyrtolite mentioned above. A letter to 'Nature' was published to this effect, but in the light of subsequent experience no importance can be attached to the observation. A very small quantity of air suffices to bring in the neon spectrum quite distinctly:

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* It is necessary to refer to a very perplexing case. The mineral malacone, which is a hydrous silicate of zirconium of considerable activity, was found by Ramsay and Travers ('Roy. Soc. Proc.,' vol. 60, 1897, p. 444), and subsequently by Kitchin and Winterson ('Chem. Soc. Trans.,' vol. 89, 1906, p. 1570) to contain much argon along with helium. I have failed altogether to confirm this result. Several specimens of the mineral (which came from Hitteroe, Norway) were examined, they gave nothing but a brilliant yellow helium glow, argon being practically invisible. I cannot doubt the genuineness of the specimens, for they correspond closely to those from the same locality in the Natural History Museum, South Kensington.

† 'Roy. Soc. Proc.,' A, vol. 79, p. 437.

1 c.c. is ample, and with care 1/10 c.c. is enough. In some other cases I have suspected neon, but can make no positive statement.

§ 6. *Summary of Conclusions.*

1. Helium can be detected in almost all the minerals of the earth's crust.

2. The quantity is in most cases about what might be anticipated from the traces of uranium and radium which the minerals contain. This is illustrated by the following selected results, which are given in round numbers only.

Mineral.	Helium present, c. mm. per kilo.	Helium ratio, *i.e.*, ratio of helium to uranium oxide.
Samarskite	1,500,000	14
Hæmatite	700	9
Galena...........	2	17
Quartz...........	2	10

3. Where much higher helium ratios than the above have been observed, the excess of helium can always be connected with the presence of thorium, except in one outstanding case. Thus the experiments afford no evidence in favour of helium production by radio-activity of ordinary elements.

4. The outstanding case is beryl, which contains abundance of helium, without anything approaching a sufficient radio-activity to explain its presence. This helium cannot be connected with any known constituent of beryl.

5. Igneous rocks, and probably siliceous minerals generally, contain small quantities of argon. In other minerals its quantity is negligible, at all events in comparison with the helium present. Nor is there any indication that it increases with the amount of radio-active material.